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(54) Carbon nanotube device, manufacturing method of carbon nanotube device, and electron emitting device

(57) The present invention discloses a carbon nanotube device comprising a support having a conductive surface and one or more carbon nanotubes, one of whose terminus binds to the conductive surface so that conduction between the surface and the carbon nanotube is maintained, wherein a root of the carbon nanotube where the carbon nanotube binds to the conductive surface is surrounded by a wall. Such a carbon nanotube device, having carbon nanotubes with a uniform direction of growth, can generate a large quantity of emitted electrons when it is used as an electron emission device.

FIG. 8A

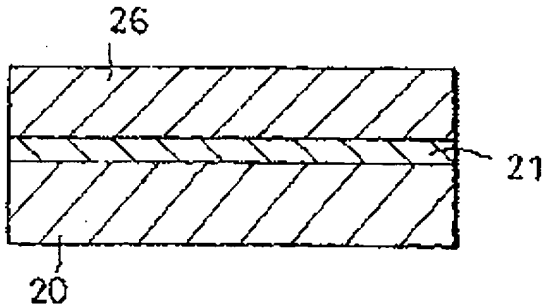

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FIG. 8B

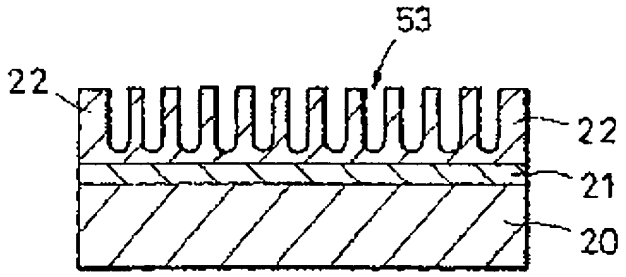


FIG. 8C

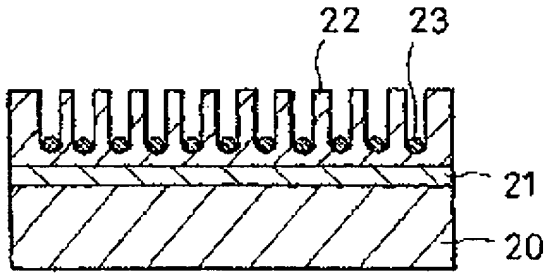
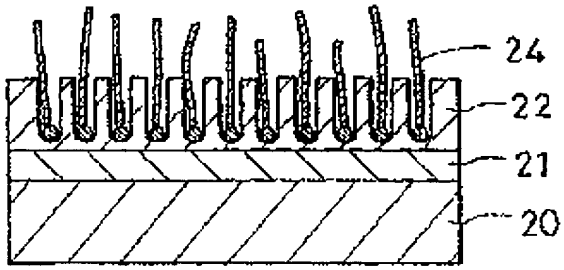


FIG. 8D



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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 8872

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	T. KYOTANI ET AL.: "Preparation of Ultrafine Carbon Tubes in Nanochannels of an Anodic Aluminum Oxide Film" CHEM. MATER., vol. 8, 1996, pages 2109-2113, XP000626894 * page 2109, right-hand column, line 1 - page 2113, right-hand column, line 34 *	1	D01F9/127 G01B7/34
A	EP 0 758 028 A (RESEARCH DEVELOPMENT CORPORATION OF JAPAN) 12 February 1997 * page 3, line 14 - page 4, line 49; claims; figure 1 *	1	
A	WO 90 07023 A (HYPERION CATALYSIS INT.) 28 June 1990 * page 2, line 14 - page 3, line 19 * * page 4, line 31 - page 8, line 6; claims *	1	
P,A	WO 98 05920 A (WILLIAM MARSH RICE UNIVERSITY) 12 February 1998 * page 8, line 4 - page 9, line 25; figure 1D *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) D01F G01B C01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 February 1999	Hellemans, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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EPO FORM 1503 03.82 (P04C01)

Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a carbon nanotube device using a carbon nanotube and a manufacturing method thereof. More particularly, the invention relates to a carbon nanotube device applicable to a functional device such as a quantum-effect device, an electronic device, a micro-machine device or a bio-device etc. Further, the invention relates to a carbon nanotube device applicable to an electron source, an STM (scanning type tunnel microscope) probe, or an ATM (atomic force microscope) probe by the utilization of sharpness of the carbon nanotube, and a manufacturing method thereof.

[0002] The invention relates also to an electron emitting device for a display, a cathode ray tube, an emitter, a lamp or an electronic gun.

Description of the Related Art

[0003] Fibrous carbon is generally called carbon fiber, and for carbon fiber that is used as a structural material having a diameter of at least several μm, several manufacturing methods have been studied. Among those studied, a method for manufacturing the carbon fiber from a PAN (polyacrylonitrile)-based fiber or a pitch-based fiber is considered to be a mainstream method.

[0004] Schematically, this method comprises making a raw material spun from a PAN fiber, an isotropic pitch or a meso-phase pitch non-meltable and hardly flammable, carbonizing the resultant material at a temperature within a range of from 800 to 1,400°C, and treating the resultant product at a high temperature within a range of from 1,500 to 3,000°C. The carbon fiber thus obtained is excellent in mechanical properties such as strength and modulus of elasticity, and for its light weight that can be used for a sporting good, an adiabatic material and a structural material for space or automotive purposes in the form of a composite material.

[0005] On the other hand, a carbon nanotube has recently been discovered having a tubular structure whose diameter is 1 μm or less. An ideal structure of the carbon nanotube is a tube formed with a sheet of carbon hexagonal meshes arranged in parallel with its tube axis. A plurality of such tubes forms a nanotube. The carbon nanotube is expected to have characteristics like metals or semiconductors, depending upon both diameter of the carbon nanotube and the bonding form of the carbon hexagonal mesh sheet. Therefore, the carbon nanotube is expected to be a functional material in the future.

[0006] Generally, carbon nanotubes are synthesized plasma.

(Carbon nanotube)

[0007] An outline of a recently developed carbon nanotube will now be described.

[0008] A material having a diameter of up to 1 μm, smaller than that of carbon fiber, is popularly known as a carbon nanotube to discriminate from carbon fiber, although there is no definite boundary between them. In a narrower sense of the words, a material having the carbon hexagonal mesh sheet of carbon substantially in parallel with the axis is called a carbon nanotube, and one with amorphous carbon surrounding a carbon nanotube is also included within the category of carbon nanotube.

[0009] The carbon nanotube in the narrower definition is further classified into one with a single hexagonal mesh tube called a single-walled nanotube (abbreviated as "SWNT"), and one comprising a tube of a plurality of layers of hexagonal meshes called a multiwalled nanotube (abbreviated as "MWNT").

[0010] Which of these types of carbon nanotube structures is available is determined to some extent by the method of synthesis and other conditions. It is however not as yet possible to produce carbon nanotubes of the same structure.

[0011] These structures of a carbon nanotube are briefly illustrated in Figs. 1A to 4B. Figures 1A, 2A, 3A and 4A are schematic longitudinal sectional views of a carbon nanotube and carbon fiber, and Figures 1B, 2B, 3B and 4B are schematic sectional views illustrating transverse sections thereof.

[0012] The carbon fiber has a shape as shown in Figs. 1A and 1B in which the diameter is large and a cylindrical mesh structure in parallel with its axis has not grown. In the gas-phase pyrolysis method using a catalyst, a tubular mesh structure is observed in parallel with the axis near the tube center as shown in Figs. 2A and 2B, with carbon of irregular structures adhering to the surrounding portions in many cases.

[0013] Application of the arc discharge process or the like gives an MWNT in which a tubular mesh structure in parallel with its axis grows at the center as shown in Figs. 3A and 3B, with a slight amount of amorphous carbon adhering to surrounding portions. The arc discharge process and the laser deposition process tend to give an SWNT in which a tubular mesh structure grows as shown in Figs. 4A and 4B.

[0014] The following three processes are now popularly used for the manufacture of the aforementioned carbon nanotube: a process similar to the gas-phase growth process for carbon fiber, the arc discharge process and the laser evaporation process. Apart from these three processes, the plasma synthesizing process and the solid-phase reaction process are known.

(1) Pyrolysis process using catalyst

[0016] This process is substantially identical with the carbon fiber gas-phase growth process. The process is described in C. E. Snyders et al., International Patent No. WO89/07163 (International Publication Number). The disclosed process comprises the steps of introducing ethylene or propane with hydrogen into a reactor, and simultaneously introducing super-fine metal particles. Apart from these raw material gases, a saturated hydrocarbon such as methane, ethane, propane, butane, hexane, or cyclohexane, and an unsaturated hydrocarbon such as ethylene, propylene, benzene or toluene, acetone, methanol or carbon monoxide, containing oxygen, may be used as a raw material.

[0017] The ratio of the raw material gas to hydrogen should preferably be within a range of from 1:20 to 20:1. A catalyst of Fe or a mixture of Fe and Mo, Cr, Ce or Mn is recommended, and a process of attaching such a catalyst onto fused alumina is proposed.

[0018] The reactor should preferably be at a temperature within a range of from 550 to 850°C. The gas flow rate should preferably be 100 sccm per inch diameter for hydrogen and about 200 sccm for the raw material gas containing carbon. A carbon tube is generated in a period of time within a range of from 30 minutes to an hour after introduction of fine particles.

[0019] The resultant carbon tube has a diameter of about 3.5 to 75 nm and a length of from 5 to over 1,000 times as long as the diameter. The carbon mesh structure is in parallel with the tube axis, with a slight amount of pyrolysis carbon adhering to the outside of the tube.

[0020] H. Dai et al. (Chemical Physico Letters 260, 1996, p. 471-475) report that, although at a low generating efficiency, an SWNT is generated by using Mo as a catalytic nucleus and carbon monoxide gas as a raw material gas, and causing a reaction at 1,200°C.

(2) Arc discharge process

[0021] The arc discharge process was first discovered by Iijima, and details are described in Nature (vol. 354, 1991, p. 56-58). The arc discharge process is a simple process of carrying out DC arc discharge by the use of carbon rod electrodes in an argon atmosphere at 100 Torr. A carbon nanotube grows with carbon fine particles of 5 to 20 nm on a part of the surface of the negative electrode. This carbon tube has a diameter of from 4 to 30 nm and a length of about 1 μm, and has a layered structure in which 2 to 50 tubular carbon meshes are laminated. The carbon mesh structure is spirally formed in parallel with the axis.

[0022] The pitch of the spiral differs for each tube and for each layer in the tube, and the inter-layer distance in the case of a multi-layer tube is 0.34 nm, which substantially agrees with the inter-layer distance of graph-

[0023] T. W. Ebbesen et al. describe conditions for generating carbon nanotubes in a large quantity by the arc discharge process in Nature (vol. 358, 1992, p. 220-222). A carbon rod having a diameter of 9 mm is used as a cathode and a carbon rod having a diameter of 6 mm, as an anode. These electrodes are provided opposite to each other with a distance of 1 mm in between in a chamber. An arc discharge of about 18 V and 100 A is produced in a helium atmosphere at about 500 Torr.

[0024] At 500 Torr or under, the ratio of the carbon nanotubes is rather low, and at over 500 Torr, the quantity of generation decreases as a whole. At 500 Torr which is the optimum condition, the ratio of carbon nanotubes reaches 75%.

[0025] The collection ratio of carbon nanotubes is reduced by causing a change in supplied power or changing the atmosphere to argon one. More nanotubes are present near the center of the carbon rod.

(3) Laser evaporation process

[0026] The laser evaporation process was first reported by T. Guo et al. in Chemical Physics Letters (243, 1995, p. 49-54), and further, generation of a rope-shaped SWNT by the laser evaporation process is reported by A. Thess et al. in Science (vol. 273, 1996, p. 483-487).

[0027] First, a carbon rod formed by dispersing Co or Ni is placed in a quartz tube, and after filling the quartz tube with Ar at 500 Torr, the entire combination is heated to about 1,200°C. Nd-YAG laser is condensed from the upstream end of the quartz tube to heat and evaporate the carbon rod. Carbon nanotubes are thus accumulated in the downstream end of the quartz tube. This process is hopeful for selective preparation of SWNTs, and has a feature that SWNTs tend to gather to form a rope shape.

[0028] The conventional art will now be described in terms of application of the carbon nanotube.

(Application of carbon nanotube)

[0029] While no applied product of carbon nanotube is available at present, active research efforts are being made for its applications. Typical examples of such efforts will be briefly described.

(1) Electron emission source

[0030] The carbon nanotube, having a shape leading end and being electrically conductive, is adopted in many research subjects.

[0031] W. A. De Heer et al. refined a carbon nanotube obtained by the application of the arc discharge process, and placed it upright on a support via a filter to use it as

tion of carbon nanotubes, and an emission current of at least 100 mA was stably obtained by the impression of 700 V from an area of 1 cm^2.

[0032] A. G. Rinzler et al. evaluated properties by attaching an electrode to a carbon nanotube obtained by the arc discharge process, and there was available an emission current of about 1 nA from a carbon nanotube with a closed end, and of about 0.5 μA from a carbon nanotube with an open end, by the impression of about 75 V (Science, vol. 269, 1995, p. 1550).

(2) STM, AFM

[0033] H. Dai et al. report, in Nature (384, 1996, p. 147), an application of a carbon nanotube to STM and AFM. According to their report, the carbon nanotube prepared by the arc discharge process was an SWNT having a diameter of about 5 nm at the leading end. Because of a thin tip and flexibility, even the bottom of a gap of a sample could be observed, and there was available an ideal tip free from a tip crash.

(3) Hydrogen storing material

[0034] A. C. Dillon et al. report, in Nature (vol. 386, 1997, p. 377-379), that the use of an SWNT permits storage of hydrogen molecules of a quantity several times as large as that available with a carbon generated from a pitch-based raw material. While their study on application has just begun, it is expected to serve as a hydrogen storing material for a hydrogen car or the like.

[0035] In the configuration and manufacturing method of a carbon nanotube in the conventional art, diameters and directions of resultant carbon nanotubes are very random, and after growth, an electrode is not connected to the carbon nanotube. More specifically, upon application of the carbon nanotube, it is necessary to collect after synthesis for purifying, and form it into a particular shape in compliance with the shape for application.

[0036] For example, when it is to be used as an electron source, A. G. Rinzler et al. teaches the necessity to take out a carbon fiber and to bond an end thereof to an electrode, as reported in Science (vol. 269, 1995, p. 1550-1553).

[0037] Further, as reported in Science (vol. 270, 1995, p. 1179-1180) and Science (vol. 1, 268, 1995, p. 845-847), Walt A. de Heer et al. discloses the necessity to provide a step of purifying a carbon nanotube prepared by the arc discharge process, and then placing upright the carbon nanotube on a support by the use of a ceramic filter. In this case, an electrode is not positively bonded to the carbon nanotube. Further, the carbon nanotubes in application tend to get entangled with each other in a complicated manner, and it is difficult to obtain devices fully utilizing characteristics of the individual carbon nanotubes.

SUMMARY OF THE INVENTION

[0038] The present invention was developed in view of the problems as described above, and has an object to provide a carbon nanotube device, in which a carbon nanotube has a strong directivity, giving a large quantity of electron emission when it is used, for example, as an electron emission device.

[0039] Another object of the invention is to provide a manufacturing method of carbon nanotube device in which the carbon nanotube binds to a conductive surface so that conduction is maintained therebetween, and the carbon nanotube has a high directivity.

[0040] Further, the invention has an object to provide an electron emission device giving a large quantity of electron emission and having a high performance.

[0041] Specifically, there is provided a carbon nanotube device comprising a support having a conductive surface and a carbon nanotube, one of whose terminus binds to said conductive surface at a site so that conduction between said conductive surface and said carbon nanotube is maintained, wherein a root of said carbon nanotube where said carbon nanotube binds to said conductive surface is surrounded by a wall.

[0042] Forming the barrier with a layer containing alumina or silicon is preferable with a view to achieving a higher density of the carbon nanotubes binding to the conductive surface. The wall containing alumina is available, after forming an aluminum thin film on the conductive surface, for example, by anodically oxidizing aluminum. At this point, the conductive surface should preferably comprises a layer containing at least one element selected from the group consisting of titanium, zirconium, niobium, tantalum, molybdenum, copper and zinc. It is not necessary that the conductive surface be previously protected even during anodic oxidation of the aluminum thin film.

[0043] There is also provided, a manufacturing method of a carbon nanotube device comprising a support having a conductive surface and a carbon nanotube, one of whose terminus binds to said conductive surface at a site so that conduction between said conductive surface and said carbon nanotube is maintained, wherein a root of said carbon nanotube at the site where said carbon nanotube binds to said conductive surface is surrounded by a wall, said method comprising the steps of:

(i) forming a plurality of carbon nanotube binding sites isolated from each other by walls on said conductive surface; and
(ii) forming carbon nanotubes at the sites.

[0044] Additionally, there is provided an election emitting device comprising:

a carbon nanotube device, which itself comprises a

ductive surface so that conduction between said conductive surface and said carbon nanotube is maintained, wherein a root of said carbon nanotube where said carbon nanotube binds to said conductive surface is surrounded by a wall;

an electrode located at a position opposite to said conductive surface; and

means for impressing a potential to a space between said conductive surface and said electrode.

[0045] According to the invention as described above, it is possible to control growth direction of the carbon nanotube by means of the wall. As a result, it is possible to provide an electron emitting device having excellent electron emitting properties, and a carbon nanotube device suitable for a probe of an STM or an AFM which gives a satisfactory image and has a high strength.

[0046] In the case where the wall comprises a layer containing alumina or silicon, it is possible to efficiently form a carbon nanotube device having a configuration in which a plurality of carbon nanotubes bind to the conductive surface, and binding sites of the individual carbon nanotubes are isolated from each other by the wall. The device of the invention, provided with carbon nanotubes whose growth directions are almost the same, and each of which have a uniform directivity isolated from each other at a high density, is suitably applicable for an electron emitting device or a probe such as an STM or an AFM.

[0047] When the conductive surface comprises a layer containing at least one material selected from the group consisting of titanium, zirconium, niobium, tantalum, molybdenum, copper and zinc, it is possible to easily form a carbon nanotube of the invention. More specifically, an alumina thin film having a narrow hole is formed through anodic oxidation also when forming the barrier by anodic oxidation of an aluminum thin film. The anodic oxidation carried out so that the bottom of the narrow hole serves as the electrode surface never damages the conductive surface, and as a result, it is possible to easily form a carbon nanotube binding conductively to the conductive surface.

[0048] In the various features of the present invention as described above, the expression "a terminus of the carbon nanotube binds conductively to the conductive surface of the support" include, in addition to the embodiment in which the carbon nanotube binds directly to the conductive surface, an embodiment in which the carbon nanotube is conductively connected to the conductive surface under a tunnel effect via an insulating layer, and an embodiment in which the carbon nanotube binds conductively to the conductive surface through an insulating layer including a path containing an element composing the conductive surface.

BRIEF DESCRIPTION OF THE DRAWINGS

various structures of a carbon nanotube: Figs. 1A and 1B respectively illustrate schematic longitudinal and transverse sectional views of an isotropic carbon fiber; Figs. 2A and 2B respectively illustrate schematic longitudinal and transverse sectional views of a carbon nanotube with amorphous carbon therearound; Figs. 3A and 3B respectively illustrate schematic longitudinal and transverse sectional views of a multi-walled nanotube; and Figs. 4A and 4B respectively illustrate schematic longitudinal and transverse sectional views of a single-walled nanotube;

Fig. 5A to 5D cover schematic conceptual views illustrating configurations of carbon nanotube devices: Fig. 5A is an example of a configuration with a different support, conductive surface layer and wall; Fig. 5B is a configuration in which a support and a layer forming a conductive surface form a single body; Fig. 5C is a configuration in which a layer composing a conductive surface and a wall form a single body; and Fig. 5D is a configuration in which a support, a layer comprising a conductive surface and a wall form a single body;

Figs. 6A to 6D covers schematic conceptual views illustrating configurations of tunnel junction type carbon nanotube devices: Fig. 6A is a configuration in which a support, a layer composing a conductive surface, an insulating layer and a wall are different; Fig. 6B is a configuration in which an insulating layer is present on the surface of a wall; Fig. 6C is a configuration in which an insulating layer is present on a part of the surface of a layer composing a conductive surface; and Fig. 6D is a configuration in which a support, a layer composing a conductive surface, and a wall form a single body;

Fig. 7 is a schematic view illustrating a carbon nanotube growing apparatus;

Figs. 8A to 8D are schematic process diagrams illustrating a manufacturing process of an upright type carbon nanotube device using alumina narrow holes;

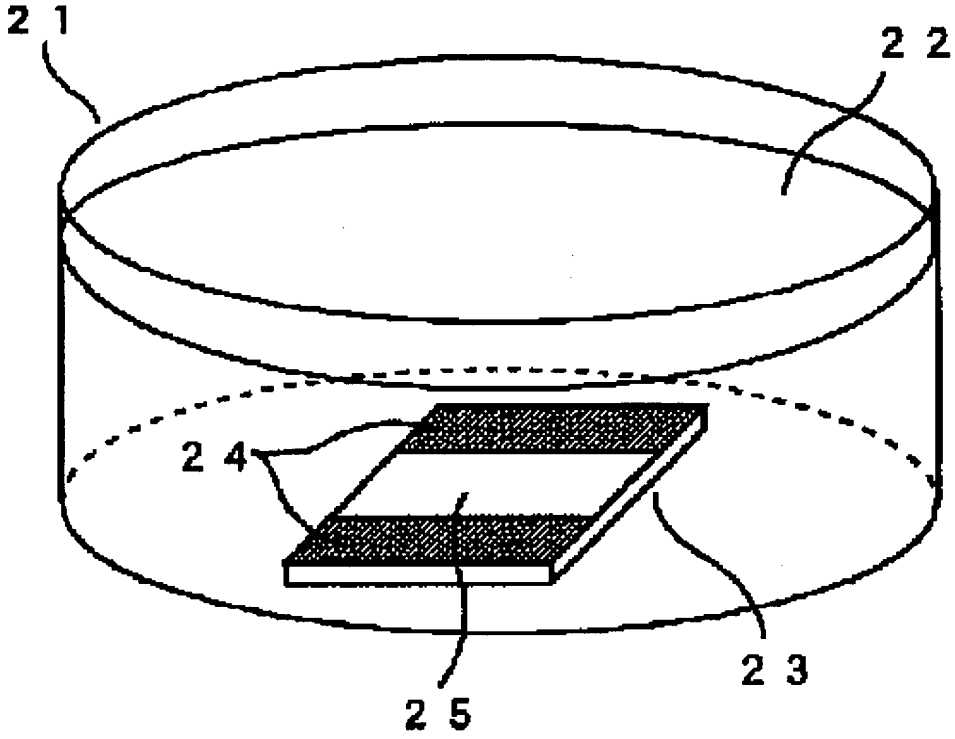
Figs. 9A to 9C are schematic process diagrams illustrating a manufacturing process of an upright type carbon nanotube device using Si narrow holes;

Figs. 10A to 10D are schematic process diagrams illustrating a manufacturing process of a tip type carbon nanotube device;

Fig. 11A is a schematic plan view of an embodiment of the tunnel type carbon nanotube device; and Fig. 11B is a sectional view of the tunnel type carbon nanotube device shown in Fig. 11A cut along the line A-A;

Fig. 12 is a schematic sectional view of another embodiment of the carbon nanotube device of the invention;

Fig. 13 is a schematic view illustrating a change in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2 4
2 3
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